Coupled Spin-Phonon Excitations in Helical Multiferroics

Chenglong Jia and Jamal Berakdar

Institut für Physik, Martin-Luther-Universität Halle-Wittenberg, 06099 Halle, Germany

Abstract

Both the Dzyaloshiskii-Moriya interaction and the exchange-striction are shown to affect dynamically the magnetoelectric excitations in the perovskite multiferroic $\mathrm{RMnO_3}$. The exchange-striction results in a biquadratic interaction between the spins and the transverse phonons, giving rise to quantum fluctuations of the ferroelectric polarization $\mathbf{P}$. This leads to low-lying phonon modes that are perpendicular to $\mathbf{P}$ and to the helical spins at small wave vector but are parallel to $\mathbf{P}$ at a wave vector close to the magnetic modulation vector. For spin-1/2 helimagnet, the local polarization can be completely reversed by the spin fluctuation, and so does the direction of the on-site spin chirality, which allows for a finite differential scattering intensity of polarized neutrons from a cycloidal magnet.

PACS numbers: 78.67.-n, 71.70.Ej, 42.65.Re, 72.25.Fe

I. INTRODUCTION

Details of the coupling mechanisms of the magnetic and the ferroelectric order in multiferroics is currently under active research. This is due to the fundamental physics involved and to promising technological applications [1]. Our focus here is the perovskite multiferroics $RMnO_3$ with R = Tb, Dy, Gd and $Eu_{1-x}Y_x$ that have incommensurate spiral spin structure [2]. The experimental finding is that $RMnO_3$ has a helical magnetic order and a finite ferroelectric (FE) polarization. The driving mechanisms of this ordering is an interplay between the exchange interaction and the Dzyaloshiskii-Moriya (DM) interaction. Specifically, the spin-orbit coupling with a strength α related to the $d(p)$-orbitals of the magnetic(oxygen) ions results in the FE polarization [3, 4] $\mathbf{P} = \alpha \hat{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j)$. $\hat{e}_{ij}$ is a unit vector connecting the sites i and j. Generally, it is to be expected that the magnetoelectric (ME) coupling will affect not only the material static properties but also the dynamical response. Based on the spin-current model, the dynamical properties of DM interaction were studied in Ref.[5–7]. A novel magnon-phonon excitations so-called electromagnon, was theoretically predicted. When the spiral plane rotates with respected to the axis of the helical wave vector, so does the the induced electric polarization, which couples the magnetic excitation to the electric field E of the radiation in the direction perpendicular to the spin spiral plane [5]. Experimental observations in $RMnO_3$ [8] and $Eu_{0.75}Y_{0.25}MnO_3$ [9] seems to be consistent with this finding. However, a detailed study of the terahertz spectrum of $Eu_{1-x}Y_xMnO_3$ [10] revealed that infrared-absorption along the spontaneous polarization direction is also possible, which is not explained by theory mentioned above. This violation suggests that the static and the dynamic ME coupling may be different [11]. We carried out a detailed investigations of the dynamical properties of the multiferroics and find that both, the DM interaction and the (super)exchange striction play an essential role and need to be taken into account.

II. THEORETICAL MODEL

We consider a one-dimensional spin chain along the z-axis with a frustrated spin interaction. An effective model that captures the spin-phonon coupling [5, 12] has the Hamiltonian

$$
\begin{aligned}
H &= H_s + H_{DM} + H_p \qquad (1)\\
H_s &= \sum_{\langle ij\rangle_{nn}} J_1(r_i - r_j) S_i \cdot S_j \\
&\quad + \sum_{\langle lm\rangle_{nnn}} J_2(r_l - r_m) S_l \cdot S_m \\
H_{DM} &= -\lambda \sum_i \mathbf{u}_i \cdot [\hat{e}_z \times (S_i \times S_{i+1})] \\
H_p &= \frac{k}{2} \sum_i \mathbf{u}_i^2 + \frac{1}{2M} \sum_i \mathbf{P}_i^2
\end{aligned}
$$

where the notation $\langle ij\rangle_{nn}$ indicates nearest-neighboring (nn) i and j, and $\langle lm\rangle_{nnn}$ corresponds the next-nearest-neighboring (nnn) l and m. The competition between the nn ferromagnetic interaction ($J_1 < 0$) and the nnn antiferromagnetic interaction ($J_2 > 0$) leads to magnetic frustration and realizes a spiral spin ordering with the wave vector $\cos Q = -J_1/4J_2$ [13–15]. H_p describe optical phonons. The spin-phonon interaction H_{DM} originates from a spin-orbital coupling and breaks the inversion symmetry along the chain. Minimizing the energy yields the condition of the atomic displacement and the local spin-configuration, $\mathbf{u}_i = \frac{\lambda}{k}\hat{e}_z \times (\mathbf{S}_i \times \mathbf{S}_{i+1})$. Particularly, if the zx helical spins along the chain, *i.e.* $\mathbf{S}_i = S(\sin iQ, 0, \cos iQ)$, an uniform electric polarization $\mathbf{P}$ along the x direction is induced by the condensation of the transverse optical (TO) phonons, $\mathbf{P} = e^*\mathbf{u}_0 = -e^*\frac{\lambda S^2}{k}\sin Q\hat{e}_x$ with a Born charge e^*. Generally, $\mathbf{u}_x$ cannot be softened through the hybridization between the TO phonons and the magnons because of $k/M \gg JS$. The spontaneous FE polarization $\mathbf{P}_x$ is frozen at $-e\mathbf{u}_0$ in the ferroelectric phase. However, after accounting for the superexchange striction, we have transverse acoustic (TA) phonons, which induces the fluctuation of the polarization hybridized with the spin bosons and soften thus the transverse phonon behavior.

Considering small atomic displacements perpendicular to the chain, $\mathbf{u}_i^{\perp} \cdot \hat{e}_z = 0$, the exchange energy J falls off as a power law with the separation of the magnetic ions

$$
J_{1,2}(|\mathbf{r}_i - \mathbf{r}_j|) \approx J_{1,2}[1 - \frac{\gamma_{1,2}}{2}(\mathbf{u}_i^{\perp} - \mathbf{u}_j^{\perp})^2] \qquad (2)
$$

where γ is in the range of $6 - 14$ [16]. The emerging TA phonon mode is coupled to the spins with the bi-quadratic interaction $-\gamma_{1,2}J_{1,2}(\mathbf{u}_i^{\perp} - \mathbf{u}_j^{\perp})^2(\mathbf{S}_i \cdot \mathbf{S}_j)$. This dynamical coupling does not contribute any additional static electric polarization but induces the fluctuation of the

electric dipole moment due to the low frequency excitation modes of TA phonon. We write explicitly the atomic displacements into two parts: (i) the statical part $\mathbf{u}_i = (u_0^x, 0, 0)$ and (ii) the dynamical part $\delta\mathbf{u}_i = (-\delta u_i^x, \delta u_i^y, 0)$. Retaining terms up to the second order in the quantum fluctuation, the spin-current model delivers the following coupling terms

$$\begin{aligned}\tilde{H}_{DM} = & -\lambda S \cos Q \sum_i \delta u_i^x (\tilde{S}_{i+1}^x - \tilde{S}_i^x) \\ & -\lambda S \sum_i \delta u_i^y (\tilde{S}_i^y \cos Q_{i+1} - \tilde{S}_{i+1}^y \cos Q_i)\end{aligned} \tag{3}$$

in the rotated spin frame: $S_i^x = \tilde{S}_i^x \cos iQ + \tilde{S}_i^z \sin iQ$, $S_i^y = \tilde{S}_i^y$, and $S_i^z = -\tilde{S}_i^x \sin iQ + \tilde{S}_i^z \cos iQ$.

III. RESULTS AND ANALYSIS

In spin-1/2 multiferroics, such as $LiCu_2O_2$ [14], the spin fluctuations may spontaneously reverse the local spin. Defining the vector of spin chirality as the average of the outer product of two adjacent spins $\hat{c}_i = (s_i \times s_{i+1})/|s_i \times s_{i+1}|$, in the $RMnO_3$-type multiferroics the direction of local FE polarization is determined by the on-site spin chirality. The dynamical DM interaction Eq.(3) yields the coupling term between the spin and the spin-chirality in the spin-1/2 multiferroics, $\sum_i \hat{c}_i^x (\hat{s}_{i+1}^x - \hat{s}_i^x) = \sum_i \hat{s}_i^x (\hat{c}_{i-1}^x - \hat{c}_i^x)$, which indicates that when the spin at site i is flipped, $\hat{s}_i \to -\hat{s}_i$, the direction of spin-chirality $\hat{c}_i$ and $\hat{c}_{i-1}$ are also reversed. Assuming all spins point along their corresponding classical directions in the ground state of the spin-1/2 helical magnet as in $NaCu_2O_2$, where a $J_1 - J_2$ spin model provides a good description of the helix state [15]. So the spin interaction can be ferromagnetically given as $-J_s(Q)\hat{s}_i \cdot \hat{s}_j$ where Q is taken as the pitch angle along the chain. An effective model that describes the interplay between the helical spin and spin-chirality has the form

$$H_{sc} = -\sum_{i,j} (J_s \hat{s}_i \cdot \hat{s}_j + J_c \hat{c}_i \cdot \hat{c}_j) - \gamma \sum_i \hat{s}_i^x (\hat{c}_{i-1}^x - \hat{c}_i^x). \tag{4}$$

The Hilbert space can be considered as the tensor product space $|i\rangle \to |s_i^z\rangle_s \otimes |c_i^z\rangle_c$. Now if the spin at site i is flipped, the spin and spin-chirality excitations are mixed due to the spin-phonon coupling. The expected value of spin-chirality is given by

$$\langle \hat{c} \rangle = 1 - \langle \hat{s} \rangle, \tag{5}$$

which is less than one. The experimental data for a finite differential scattering intensity of polarized neutrons from $LiCu_2O_2$ [14] suggests $\langle \hat{c} \rangle \approx 0.3$ which is consistent with the estimated value $\langle \hat{c} \rangle = 0.44$ based on the ordered moment, $0.56\mu_B$ per magnetic copper site [15].

For magnet $RMnO_3$, the helical spin ordering occurs, corresponding to the condensation of the spin bosons. By using the standard linear-spin-wave approximation, a dynamical magon-phonon interaction reads,

$$\tilde{H}_{DM} = -\lambda S \cos Q \sum_q \delta u_q^x \tilde{S}_q^x (\cos q - 1) \\ -\lambda S \sum_q \delta u_q^y \tilde{S}_{q\pm Q}^y (e^{\mp iQ} - e^{i(q\pm Q)})/2 \tag{6}$$

δu_q^y is hybridized with the spin at $q \pm Q$ (optical magnons), but δu_q^x is coupled to $\tilde{S}^x$ at q (acoustical magnons). The polarization correlation functions are given as

$$\ll \delta u_q^x | \delta u_{\bar{q}}^x \gg = \frac{\omega^2 - \omega_s^2}{M[\omega^4 - \omega^2(\omega_p^2 + \omega_s^2) + \omega_p^2(\omega_s^2 - \omega_{sp}^2)]}, \\ \ll \delta u_q^y | \delta u_{\bar{q}}^y \gg = \frac{1}{M[\omega^2 - \omega_p^2 + \frac{\lambda^2 S^3}{2M} \sum_{q'=q\pm Q} G_s(q')]}.$$

where ω_p is the frequency for the transverse phonon, $\omega_s(q)$ is the energy dispersion of the spin-excitation, $\omega'_{sp}(q) = [2(A(q) - 2B(q))(\lambda^2 S^3 \cos^2 Q(1 - \cos q))/k']^{1/2}$, and $G_s(q \pm Q) = (A(q \pm Q) + 2B(q \pm Q))(1 - \cos(q \pm 2Q)/(\omega^2 - \omega_s(q \pm Q))$ with

$$A(q) = -J_1[\cos Q + \frac{1}{2}(1 + \cos Q)\cos q] \\ - J_2[\cos 2Q + \frac{1}{2}(1 + \cos 2Q)\cos 2q] \\ + \frac{\lambda^2 S^2 \sin^2 Q}{2k}(2 - \cos q) \tag{7}$$

$$B(q) = \frac{J_1}{4}(1 - \cos Q)\cos q + \frac{J_2}{4}(1 - \cos 2Q)\cos 2q \\ - \frac{\lambda^2 S^2 \sin^2 Q}{4k}\cos q \tag{8}$$

At small wave vectors, $q \sim 0$ and $\omega_p \approx \sqrt{k/M}$, the TA phonon is decoupled from spins. The antisymmetric DM interaction dominates over the spin-phonon coupling. δu_0^y is coupled via $(\tilde{S}_Q^y - \tilde{S}_{\bar{Q}}^y)$ to the rotation of the spin plane and the direction of the polarization along the chain. However, at a wave vector close to the magnetic modulation vector, i.e. $q \sim Q$, both the symmetric and antisymmetric magnetoelectric interaction respond to the fluctuations

of the polarization. Especially, in the direction parallel to the FE polarization $\mathbf{P}$, there is a low frequency range around $\omega^x_- \cong \omega_s(Q)$ where u^x couples resonantly to light. Introducing an easy-plane spin anisotropy $D(S_y)^2$ into the spin system, we observe nearly the same low-frequency behavior of the polarization correlation functions $\omega^x_- \approx \sqrt{JSD} \approx \omega^y_-$. These conclusions are also qualitatively consistent with experiment observations for $Eu_{1-x}Y_xMnO_3$ [10].

IV. SUMMARY

In conclusion, we studied the origin of the magnetoelectric dynamics in the orthorhombic perovskite $RMnO_3$. At a small wave vector, the DM interaction determines the low-frequency behavior of the phonons. For a wave vector close to that of the magnetically modulated structure, the exchange striction induces fluctuations in the FE polarization, and additional low-lying mode parallel to the FE polarization emerges. Due to the dynamical Dzyaloshiskii-Moriya interaction, the spin-chirality is strongly coupled to the spin fluctuation which implies a large quantum flucatuation of the spin-chirality in the ordered spin-1/2 system and results in a finite scattering intensity of polarized neutrons from a cycloidal helimagnet.

Acknowledgement: This work is supported by the German Science Foundation DFG through SFB762 -B7- *functionality of oxide interfaces*.

[1] Y. Tokura, Science **312**, 1481 (2006); S.-W. Cheong and M. Nostovoy, Nat. Mater. **6**, 13 (2007).

[2] T. Kimura *et al.*, Nature (London) **426**, 55 (2003); T.Goto *et al.*, Phys. Rev. Lett. **92**, 257201 (2004). M. Kenzelmann *et al.*, Phys. Rev. Lett. **95**, 087206 (2005); Y. Yamasaki *et.al.*, Phys. Rev. Lett. **96**, 207204 (2006); J. Hemberger *et.al.*, Phys. Rev. B **75**, 035118 (2007).

[3] H. Katsura, N. Nagaosa, and A. V. Balatsky: Phys. Rev. Lett. **95**, 057205 (2005); I.A. Sergienko and E. Dagotto, Phys. Rev. B **73**, 094434 (2006).

[4] C. Jia, S. Onoda, N. Nagaosa, and J.-H. Han, Phys. Rev. B **74** 224444 (2006); Phys. Rev. B **76** 144424 (2007).

[5] H. Katsura, A. V. Balatsky, and N. Nagaosa, Phys. Rev. Lett. **98**, 027203 (2007).

[6] I.E. Chupis, Low. Temp. Phys. **33**, 715 (2007); A. cano, and E. I. Kats, Phys. Rev. B **78**, 012104 (2008).

[7] A. Pimenov, T. Rudolf, F. Mayr, A. Loidl, A. A. Mukhin, and A. M. Balbashov, Phys. Rev. B **74**, 100403(R) (2006).

[8] A. Pimenov1, A. A. Mukhin, V. Yu. Ivanov, V. D. Travkin, A. M. Balbashov and A. Loidl, Nat. Phys. 2, 97 (2006);

[9] R. Valdes Aguilar, A. B. Suchkov, C.L. Zhang, Y. J. Choi, S.W. Cheong, and H. D. Drew, Phys. Rev. B **76** 060404(R) (2007).

[10] A. Pimenov, A.Loidl, A.A. Mukhin, V. D. Travkin, V.Yu. Ivanov, and A. M. Balbashov, Phys. Rev. B **77** 014438 (2008).

[11] Y. Takahashi *et al.*, Phys. Rev. Lett. **101**, 187201 (2008); R. Valdés Aguilar *et al.*, Phys. Rev. Lett. **102**, 047203 (2009).

[12] C. Jia and J. Berakdar, Eur. Phys. Lett. **88**, 57004 (2009).

[13] T. Kimura *et al.*, Phys. Rev. B **68**, 060403(R) (2003).

[14] S. Park *et al.*, Phys. Rev. Lett. **98**, 057601 (2007); S. Seki *et al.*, Phys. Rev. Lett. **100**, 127201 (2008).

[15] L. Capogna, M. Mayr, P. Horsch, M. Raichle, R. K. Kremer, M. Sofin, A. Maljuk, M. Jansen, and B. Keimer, Phys. Rev. B **71**, 140402(R) (2005).

[16] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Dover, New York, 1980).